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(57) Abstract

The invention is related to an antimicrobic composition whose antimicrobic component contains: a) about 50-99.8 weight % of unsubstituted or substituted C_1-C_4 monocarboxylic acid, and b) about 0.2-30 weight % of the ester or unsubstituted or substituted benzoic acid. The composite of the carboxylic acid and the ester of benzoic acid yields better results than when using, e.g., benzoic acid. The composition according to the invention can also contain a carrier in particle form in which the said antimicrobic component has been absorbed.

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ANTIMICROBIC COMPOSITION AND ITS USE

The invention is related to an antimicrobic composition and its use as a substance inhibiting the growth of detrimental microbes.

One significant quality-improving factor in food stuffs and in beef cattle and poultry forage is that they are free from *Salmonella, Listeria, E. coli* and other bacteria which cause food poisoning. Abundant use of antibiotics in controlling bacteria is not recommended because it results in the growth of resistant bacterial populations. Therefore, it is desired to discover improved preservatives.

According to the publication **Poultry International**, July 1994, pp. 40-42, mixtures of organic acids, particularly propionic acid and formic acid, or mixtures of organic acids and their ammonium salts, or salts of organic acids are used to prevent Salmonella in poultry forage. The products are either solutions or solids.

The publication Applied and Environmental Microbiology, Aug. 1980, 352-357 discloses that benzoates and their derivatives have been widely used as antimicrobials. Their effect increases with increased acidity, implying that the free acid works as an active ingredient.

The effect of propionic acid, acetic acid, sorbic acid, and benzoic acid and mixtures thereof are known from mould control of moist feed grain (Poultry Science 60 (1981), 2182-2188).

The publication Food Microbiology, 5 (1988) : 3, pp. 135-139 explains that a composition containing 1 % acetic acid, 1 % lactic acid, maleic acid, tartaric acid, or citric acid, 0.05 % sorbic acid, 0.05 % benzoic acid, and 3.5 % salt, acts, in a salad whose pH is buffered to 4.8, as a bactericide with respect to *Salmonella blockley, Escherichia coli,* and *Staphylococcus aureus*, and is bacteriostatic with respect to *Streptococcus Faecalis*.

The publication WO 92/21239 discloses an antimicrobic composition against, e.g., *Salmonella*, containing a polyunsaturated C_5-C_{14} monocarboxylic acid, such as sorbic acid or its derivative, together with a substituted or an unsubstituted aromatic carboxylic acid, such as benzoic acid or its salt or ester. The compositions may also

contain organic or inorganic acids. Formic acid is not presented among the numerous acids listed in the publication.

The publication International Journal of Food Microbiology 22 (1994) : 2-3, pp. 127-140, explains that the composition of potassium sorbate and sodium benzoate slows down or inhibits the growth of *Salmonella* in milk or cheese when its pH is regulated with propionic acid.

Esters of parahydroxylbenzoic acid, such as propylparaben, possibly together with butylated hydroxyanisole, are known to have an inhibiting effect on the growth of *Salmonella* (Proc. Int. Symp. Food Microbiol., 11th Meeting 1980, 377-84 (1981); J. Food Prot. (1980), 43(3), 191-4).

These prior art antimicrobic compositions have the disadvantage that when benzoic acid is used, its migration to microbe cells is unsatisfactory. On the other hand, when an ester of benzoic acid is used, its migration to microbe cells is satisfactory but it is not as effective as benzoic acid as an antimicrobial.

The problem of the publications described above has now been solved with the aid of a new antimicrobic composition which is mainly characterised in comprising an antimicrobic component that contains:
a) about 50-99.8 weight-% of unsubstituted or substituted C_1-C_4 monocarboxylic acid, and
b) about 0.2-30 weight-% of an ester of an unsubstituted or a substituted benzoic acid.

By using organic acid and an ester of benzoic acid together, a mixture is provided which penetrates microbe cells and forms an effective antimicrobic benzoic acid in the microbe cells. The present invention is related to compositions according to this principle in particular.

Thus it has been discovered that compositions containing C_1-C_4 monocarboxylic acid and esters of unsubstituted or substituted benzoic acid are effective in preventing *Salmonella* and other detrimental microbes and inhibiting the growth thereof.

The antimicrobic composition according to the invention comprises a first antimicrobic component consisting of a first subcomponent a) which is an

unsubstituted or substituted C_1-C_4 monocarboxylic acid. The preferred amount is about 60-98 weight-% of the weight of the anitimicrobial component. According to one embodiment, the unsubstituted or substituted C_1-C_4 monocarboxylic acid is an acid selected from: formic acid, acetic acid, propionic acid, n-butyric acid, isobutyric acid, glycolic acid, lactic acid, hydroxybutyric acid, pyruvic acid, acetacetic acid, and a mixture thereof, preferably formic acid, acetic acid, propionic acid, lactic acid or a mixture thereof, most preferably formic acid or a mixture of formic acid and propionic acid.

The antimicrobic composition according to the invention comprises an antimicrobic component consisting of a second component which is an ester of an unsubstituted or substituted benzoic acid. The antimicrobic component preferably contains about 1-20 weight-%, and preferably about 2-10 weight-% of an ester of unsubstituted or substituted benzoic acid. According to one preferred embodiment, the ester of the unsubstituted or the substituted benzoic acid is selected from esters of an unsubstituted benzoic acid and from those of a benzoic acid substituted with one or more alkyls, halogens, nitros, hydroxies, and/or aminos. Especially preferred esters comprise esters of benzoic acid or those of p-hydroxybenzoic acid.

According to one embodiment, the ester of the unsubstituted or the substituted benzoic acid is the ester of the unsubstituted or substituted benzoic acid and an alcohol which is selected from: benzoic alcohol, methanol, ethanol, n-propanol, isopropanol, n-butyl alcohol, and isobutyl alcohol. Especially preferred ester-forming alcohols include methanol, ethanol, n-propanol, and isopropanol.

Alcohols containing several hydroxyl groups that are viable for the ester of benzoic acid of the invention include, e.g., glycols, such as 1,2-propanediol, and triols, such as glycerol.

Particularly preferred esters include methyl benzoate, ethyl benzoate, n-propyl benzoate, isopropyl benzoate, methyl-p-hydroxylic benzoate, ethyl-p-hydroxylic benzoate, n-propyl-p-hydroxylic benzoate, isopropyl-p-hydroxylic benzoate, and butyl-p-hydroxylic benzoate.

The results of a laboratory test carried out indicate that the effect of the mixtures of carboxylic acid/benzoic acid esters according to the invention is at its best if the stability of the esters against hydrolysis has been suitably lowered. It has been discovered in particular that the restarting of the growth of *Salmonella* after the

treatment has been decreased in this case. Migration in forage material and through the cell walls of bacteria is probably strongest when the ester form is prevailing but the correctly-timed decomposition of esters and the resulting benzoic acid generated *in situ* in the object of use might be significant with respect to the effect of the bacterium.

It is important that, if in addition to said C_1-C_4 monocarboxylic acid component, another substance that accelerates the hydrolysis of the ester of the unsubstituted or the substituted benzoic acid is used. The preferred content of this substance is 0.2-20 weight-% of the weight of the antimicrobic component. A preferable content is 3-15 weight-%.

The advantageous embodiments of the invention thus contain activators that accelerate the decomposition of the ester. Tests have also indicated that compositions that catalyze the decomposition of esters, can also decompose carboxylic acid, formic acid in particular. Typical activators include mineral acids, such as sulphuric acid, hydrochloric acid, nitric acid, and phosphoric acid or a mixture thereof. Regarding mineral acids, hydrochloric acid is a stronger catalyser than nitric acid.

According to one embodiment, the antimicrobic component of the composition according to the invention also comprises about 0.02-20 weight-%, preferably about 0.5-10 weight-% of the ester of C_1-C_4 monocarboxylic acid that acts synergistically with the ester of the unsubstituted or the substituted benzoic acid, with C_1-C_4 alcohol. Typical such esters include methylester, ethylester or propylester of formic acid, acetic acid or propionic acid. These substances are preferably obtained when C_1-C_4 alcohol, preferably propanol, is added to the composition in situ.

In addition to the above-mentioned ingredients, the antimicrobic component may contain other compositions that improve the preservation power, such as C_4-C_{14} carboxylic acids, such as free benzoic acid, isobutyric acid or octanic acid. or corresponding alcohols; monoglycerides of C_8-C_{16} carboxylic acids or other bactericidal or bacteriostatic surface-active compositions, dicarboxylic acids, such as oxalic acid, malonic acid, succinic acid, adipic acid, pimelic acid, suberic acid, fumaric acid, or maleic acid; polykarboxylic acids, such as polyacrylic acid. or copolymeric acids formed between unsaturated compounds that are polymerised with acrylic acid and polyacrylic acid; hydroxycarboxylic acids, dicarboxylic acids or polycarboxylic acids, such as sorbic acid, ascorbic acid, cinnamic acid. salicylic

acid, tartaric acid or maleic acid; complexing agents, such as EDTA, DTPA; or derivatives, such as salts or esters, of all the above-mentioned acids. The mixture may, depending on the application of use, further contain salts affecting as preservatives, including salts of magnesium, zink and copper, compositions that adjust animal nutrients or the salt content of the mixture or that buffer its pH, including ammonium phosphate or potassium sulphate; imidiatzolindylurea, phenolic compositions and sulphonic acids, such as lignosulphonates, or aldehydes, such as formadehyde. Furthermore, components acting as antioxidants, such as butylated hydroxyanisole or hydroxytoluene, or esters of gallic acid can be added to the mixture.

In addition to C_1-C_4 monocarboxylic acids, the compositions according to the invention can also contain other compounds that react with water in an acidly manner, such as organic or inorcanig acids or polyacids, or compounds that form acids in a solution. The acids may also be in a partly neutralised form, such as ammonium salts, for instance. The compositions that form acids include inorganic or organic salts or acid anhydrides that react in an acidly manner.

Since even relatively small amounts of water decrease and, correspondingly, activators increase the decomposition of both esters and formic acid, the properties of the mixture can be modified so that a suitable level of activity and a storage stability sufficient for each application are achieved. The freezing point of the antimicrobic liquid component of the composition according to the invention is a few degrees above freezing point if its C_1-C_4 acid content is high and the water content very low at the same time. By increasing the water content, the melting point can be lowered considerably when desired. A preferred water content is about 1-30 weight-% and preferably about 5-20 weight-%.

In conventional temperatures, the preservatives according to the invention are either in the form of a solution or in a solid form. The advantages of the solid state include better security during transport, a slight smell, and an easy dispensing. According to a preferred embodiment of the invention, the composition comprises, in addition to the antimicrobic component, also a solid corpuscular carrier. In this case, it is advantageous if the weight ratio between the antimicrobic component and the corpuscular carrier is in the range of 1:10 - 10:1, preferably in the range of 3:7 - 7:3. Because the issue often is about absorbing the antimicrobic liquid component on the corpuscular carrier, the specific surface of the corpuscular carrier has to be large enough, preferably at least about 10, and more preferably at least about 100 m^2/g.

The approximate particle size of the corpuscular carrier is preferably 0.01-20 mm, most preferably about 0.1-2 mm.

The corpuscular substance mentioned above is preferably selected from the following: inorganic corpuscular substances based on silicium dioxide and/or alumina, such as siliceous earth, moler earth, silicic acid, silica, alumina, bentonite, montmorrillonite, perlite, steatite, chlorite, expanded vermiculite, calcium silicate, sodium aluminium silicate, and zeolites, inorganic salts that dissolve sparingly in water and organic acids, and organic substances such as synthetic polymers, cellulose, cellulose derivatives, lignin and lignin derivatives.

The solid composition according to the invention ranges from fairly dry to fairly moist. The former is easy to dispense also in lower temperatures, the latter may cake together in temperatures lower than the melting point of the liquid phase but when the temperature is increased, it is again easy to process. The processibility can be even improved by powdering with a fine solidifying agent or other powder.

As already mentioned before, the composition according to the invention comprises an antimicrobic substance that is preferably absorbed in the corpuscular substance. Particularly good preservative fluids include those that are easy to handle by dispensing devices, such as granular mineral absorbents, including moler earth, and lumpy celluloses.

Solic compositions are thus prepared by absorbing a composition in liquid form as such in a large-area inorganic or organic absorbent, such as silica, clay mineral, or cellulose or mixtures thereof. Solid compositions may also be prepared so that its liquid ingredients or liquid compositions of the ingredients are separately absorbed in similar or different absorbents, which are finally mixed together. At the same time, other possible solid ingredients may be added. The composition according to a particularly preferred embodiment of the invention is in a solid particle-like form so that the mineral acids and other possible compositions that unstabilize formic acid or the ester of the unsubstituted or substituted benzoic acid are situated in different particles than the formic acid and the said benzoic acid esters.

Thus the antimicrobic substance is absorbed in the first part of the corpuscular substance, and the substance that accelerates the hydrolysis of the ester of the unsubstituted or the substituted benzoic acid is absorbed in the second part of the corpuscular substance.

A particularly preferred embodiment of the antimicrobic composition according to the invention is obtained with a composition comprising:

1) an antimicrobic component comprising:

a) about 50-99.8 weight-% of unsubstituted or substituted C_1-C_4 monocarboxylic acid,

b) about 0.2-30 weight-% of the unsubstituted or the substituted ester of benzoic acid,

c) about 0-20 weight-% of a substance that causes a hydrolysis of the ester of the unsubstituted or the substituted benzoic acid,

d) about 0-20 weight-% of the ester of C_1-C_4 monocarboxylic acid with alcohol that acts synergistically with the ester of the unsubstituted or the substituted benzoic acid,

e) about 0-30 weight-% of water, and

2) a solid corpuscular carrier, whereby the weight ratio between the antimicrobic component and the solid corpuscular substance is in the range of 1:10 - 10:0.

This preferred embodiment also comprises the advantageous components and parametric relations which are presented above separately.

Lastly, the invention is related to the use of any of the compositions described above as a substance inhibiting the growth of hazardous microbes, such as *Salmonella*, in forage material and forage products and the like. In this case, it is possible to add the composition to the forage material or animal forage in the form of a processing material or an additive. The composition may also be used to preserve green forage or grain, to improve the hygiene of cattle sheds and the like, or to disinfect devices, equipment, and packages.

Some implementive and reference examples are described in the following, the sole purpose thereof being to illustrate the invention.

<u>Example 1</u> FORAGE TEST

An inoculate of *Salmonella infantis*, 1500-3000 bacteria/g of forage, was evenly mixed with a commercial forage product for feeding chickens, including about 2/3 of grain, the rest being mainly fish meal and soya. The studied preservative was spread in the infected forage as evenly as possible in an amount corresponding to a dosage of 8 kg/t. Peptone water was measured into a control bottle. The cultures were kept in 1 litre Erlenmayer bottles sealed with aluminium foil in room

temperature. 2 parallel samples of 10 g each were taken of the cultures each sampling day. Sets of dilution were made of the samples after an Ultra-Turrax mixing. 50 µl of the samples were spread from the dilution tubes on agar sheets on Petri dishes. The bacterial colonies formed after an incubation of 24 h/37° C were counted.

Example	Preservative	pH 0d/42d	The time for the Salmonella to disappear (2 parallel determinations)
Comparison	Peptone water	6.8/6.5	42 d, 42 d
Comparison	Solution 1 *)	6.2/5.8	7 d, 7 d
Comparison	95% solution 1 5% H_2SO_4	6.0/5.8	5 d, 42 d
Comparison	90% solution 1 10% H_2SO_4	5.9/5.8	7 d, 7 d
Invention	85% solution 1 10% H_2SO_4 5% ethyl benzoate	6.0/6.1	1 d, 2 d

*) 78 % formic acid, 2 % phosphoric acid, and 20 % water

Example 2 A test was conducted as in the previous example but using another forage sample. The following results were obtained:

Example	Preservative	pH	The time for the Salmonella to disappear (2 parallel determinations)
Comparison	Peptone water	6.5	19 d, 30 d
Comparison	Solution 1 *)	5.9	19 d, 19 d
Invention	85% solution 1 10% HCl 5% ethyl benzoate	6.1	5 d, 5 d

*) 78% formic acid, 2 % phosphoric acid, and 20% water

The examples show that the forage buffers the test solution so that no result is achieved in the preservative through decrease in pH.

Example 3 SALMONELLA

The *Salmonella infantis* used in the test had originally been isolated from a chicken and cultivated in buffered peptone water. For the test, sets of dilution were made in peptone water by using different amounts of preservatives. The growth of bacteria was observed by a Bioscreen device (Labsystems, Finland). The device automatically measures, from the set of samples, the cloudiness that depicts bacterial growth as a function of time. The results are presented in Figs. 1 (acetic acid) and 2 (acetic acid with 2.5 weight-% of EB and 2.5 weight-% of propyl formate). It is discernible that the growth of Salmonella is inhibited when the acetic acid content is 0.5 weight-%, but when 5 weight-% of the 1:1 ester mixture of ethyl benzoate + propyl formiate according to the invention was mixed with the acetic acid, the growth could be inhibited even with 0.3 weight-% of preservative.

Example 4A THE EFFECT OF MINERAL ACID ON STABILITY

The effect of sulphuric acid and hydrochloric acid on the stability of liquid compositions was studied. About 10 g of each composition was weighed into 100 ml bottles which were tightly sealed and kept in an increased temperature of 45° C for 10 days to accelerate the reaction. Then the amount of carbon monoxide gas generated in the gas phase of the bottles during the decomposition of the formic acid and the amount of the/ ethyl benzoate left in the solution and that of the benzoic acid generated as its breakdown product were analyzed. The results are shown below:

Composition (weight fractions)	H_2SO_4	HCl
Formic acid (99 %)	72.6	72.6
Sulphuric acid (37 %)	23.1	-
Hydrochloric acid (37 %)	-	23.1
Ethyl benzoate	4.3	4.3
After one week:		
Appearance	a clear solution	crystalline
CO, ml/bottle *)		
a)	0.91	25.8
b)	0.91	26.0
Ethyl benzoate, %		
a)	0.90	0.08
b)	0.90	0.07
Benzoic acid, %		
a)	2.73	3.51
b)	2.71	3.38

*) a) and b) are parallel samples

It is discernable that both acids activate the decomposition of both the ester and the formic acid. When hydrochloric acid was used, a considerable amount of carbon monoxide gas had formed already during one week in an incubator, and the amount of benzoic acid was so large that some of it had crystallized. This composition that is rich in hydrochloric acid is thus suitable to be used only when no preservation time is required of the product.

Example 4B

The test of Example 4A was repeated so that propyl benzoate was used instead of ethyl benzoate. The amount of propyl benzoate in the sample containing sulphuric acid was 1.68 weight fractions, and 0.14 weight fractions in the sample containing hydrochloric acid. Both solutions remained clear.

Example 5 STABILITY TEST ON A SOLID FORMULA: STRONG FORMIC ACID AND AN 85 % FORMIC ACID

Liquid mixtures were absorbed in a solid absorbent according to the next table. The obtained products were packed in impermeable bottles which were kept in increased

temperatures. The amount of carbon monoxide generated as a breakdown product of the formic acid was analyzed from the gas phase of the bottles by using gas chromatograph. The following results were obtained:

Composition, weight fractions	A	B	C	D	E	F
Solid absorbent	60	60	60	60	60	60
Formic acid (99 %)	40	-	34	-	38	
Formic acid (85 %)	-	40	-	34	-	38
H_2SO_4, strong	-	-	4	4	-	2
Ethyl benzoate	-	-	2	2	2	2
The amount of the formed CO, ml/100 g						
15 h in 60° C	0.2	0.1	3.8	0.3	-	-
36 h in 45° C	-	-	-	-	0.1	0.1

The test indicates that with sulphuric acid present, the 99 % formic acid starts to dehydrate but aqueous formic acid is distinctly more stabile.

<u>Example 6</u> PREPARATION OF SOLID ABSORBENT

59 weight fractions of granular absorbent called Damolin (Dansk Moler Industri A/S) with a particle size of 0.2-0.6 mm was dispensed to the forward end of a screw conveyor during a certain period of time by using a feeding device. During the same period of time, 41 weight fractions of an acid mixture was fed on top of the absorbent on the screw conveyor by using a pump. The acid mixture contained:

Formic acid	68.0 weight-%
Water	15.3 weight-%
Sulphuric acid	10.0 weight-%
Ethyl benzoate	5.0 weight-%
Phosphoric acid	1.7 weight-%

A fixed product was obtained which was easy to dispense.

Example 7 PREPARATION OF SOLID ABSORBENTS

The following fixed mixtures were made:

	7/1	7/2	7/3	7/4
FA:EB 95:5	40	48	70	70
Damolin	60	48	30	-
Zeothix 265	-	4	-	-
Cellulose	-	-	-	30

FA = Formic acid
EB = Ethyl benzoate

Damolin was the same as the one used in the previous example. Zeothix 265 is a precipitated silicic acid (Huber Corporation). The cellulose was commercial sheet cellulose which was used to make pieces of about 1mm x 1mm by shredding it first with a shredder to form strips, which were then fed in transversally and, finally, oversized pieces were screened out.

Mixture 7/1 was granular and easy to process. Mixture 7/2 felt dry but did not flow as easily as the former mixture. Mixture 7/3 was fine and dry, but vault-forming, and thus more difficult to dispense. Mixture 7/4 maintained its block-like form and remained relatively easy to process, even though it felt damp. The hardness of its pieces could be further improved by powdering the mixture with small amounts of a salt-like substance which form a slightly soluble formiate such as calcium or magnesium formiates. Such substances include, e.g., finely powdered calcium chloride, calcium carbonate, dolomite, and calcium sulphate.

Example 8 MINERAL ACID IN THE SAME/A DIFFERENT GRANULE

60 parts by weight of a granular absorbent was mixed with 40 parts by weight of a mixture of strong formic acid, sulphuric acid, and ethyl benzoate in a ratio of 85:10:5. Another mixture was made with a similar approximate composition by mixing together a) 90 parts by weight of a mixture containing 60 weight-% of the absorbent and 40 weight-% of a mixture of formic acid and ethyl benzoate in a ratio of 94.4:5.6, and b) 10 parts by weight of a mixture containing 40 weight-% of sulphuric acid and 60 weight-% of the absorbent. About 10 g samples of the mixtures were weighed into 100 ml bottles which were closed tightly and placed into an incubator at a temperature of 45° C for one week. The amount of carbon monoxide gas generated in the gas phase of the bottles in the breakdown reaction of

formic acid was then analyzed. The results indicate that the stability of the product can be improved considerably by placing the mineral acid in a different granule:

Sample	CO, ml/sample
Mineral acid in the same granule with formic acid and a benzoic acid ester	31.1
Mineral acid in a different granule	1.34

Example 9 PREPARATION OF A SYNERGISTIC ESTER MIXTURE

Compositions according to the following table were prepared:

Example	9/A	9/B	9/C	9/D
FA (EB)	95	85	85	75
H_2SO_4	-	-	10	10
Water	-	10	-	10
Propanol	5	5	5	5

FA(EB) : a mixture with 93.9 parts by weight of formic acid and 4.1 parts by weight of ethyl benzoate, and 0.03 parts by weight of benzoic acid.

When the samples were analyzed, it could be perceived that none of the mixtures no longer contained propanol. Instead, propyl formiate had been formed:

	9/A	9/B	9/C	9/D
Formic acid	87.5	75.4	76.5	66.7
Ethyl benzoate	4.1	3.6	3.0	2.4
Benzoic acid	0.03	0.03	0.5	0.6
Propanol	0.0	0.0	0.0	0.0
Propyl formiate	7.3	7.0	6.8	6.7

In a corresponding manner, it was possible to create propyl acetate in preservatives with acetic acid, and propyl propionate in solutions with propionic acid.

CLAIMS

1. An antimicrobic composition, **characterised** in comprising an antimicrobic component containing

a) about 50-99.8 weight-% of an unsubstituted or a substituted C_1-C_4 monocarboxylic acid, and

b) about 0.2-30 weight-% of the ester of an unsubstituted or a substituted benzoic acid.

2. A composition according to Claim 1, **characterised** in that the antimicrobic component comprises about 60-98 weight-% of an unsubstituted or a substituted C_1-C_4 monocarboxylic acid.

3. A composition according to Claim 1 or 2, **characterised** in that the unsubstituted or the substituted C_1-C_4 monocarboxylic acid is an acid selected from the following: formic acid, acetic acid, propionic acid, n-butyric acid, isobutyric acid, glycolic acid, lactic acid, hydroxybutyric acid, pyruvic acid, acetacetic acid, and a mixture thereof, preferably formic acid, acetic acid, propionic acid, lactic acid, or a mixture thereof, preferably formic acid or a mixture of formic acid and propionic acid.

4. A composition according to Claim 1, 2 or 3, **characterised** in that the antimicrobic component comprises about 1-20 weight-%, preferably about 2-10 weight-% of the ester of an unstubstituted or a substituted benzoic acid.

5. A composition according to any of the preceding Claims, **characterised** in that the ester of the unsubstituted or the substituted benzoic acid is selected from the esters of a benzoic acid that is unsubstituted and a benzoic acid that is substituted by one or more alkyls, halogens, nitros, hydroxies, and/or aminos.

6. A composition according to Claim 5, **characterised** in that the the ester of the unsubstituted or the substituted benzoic acid is selected from the esters of benzoic acid or p-hydroxybenzoic acid.

7. A composition according to any of the preceding Claims, **characterised** in that the ester of the unsubstituted or the substituted benzoic acid is the ester of the unsubstituted or the substituted benzoic acid and an alcohol that is selected from the following: benzoic alcohol, methanol, ethanol, n-propanol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol.

8. A composition according to any of the preceding Claims, **characterised** in that the ester of the unsubstituted or the substituted benzoic acid is selected from the following: methyl benzoate, ethyl benzoate, n-propyl benzoate, iso propyl benzoate, methyl-p-hydroxybenzoate, ethyl-p-hydroxybenzoate, n-propyl-p-hydroxybenzoate, isopropyl-p-hydroxybenzoate, and butyl-p-hydroxybenzoate.

9. A composition according to any of the preceding Claims, **characterised** in that the antimicrobic component comprises
c) about 0.2-20, preferably 3-15 weight-% of a substance that accelerates the hydrolysis of the ester of the unsubstituted or the substituted benzoic acid.

10. A composition according to Claim 9, **characterised** in that the substance that accelerates the hydrolysis of the ester of the benzoic acid is a mineral acid or a mineral acid mixture.

11. A composition according to any of the preceding Claims, **characterised** in that the antimicrobic component comprises
d) about 0.02-20 weight-%, preferably about 0.5-10 weight-% of the ester of C_1-C_4 monocarboxylic acid with C_1-C_4 alcohol, affecting synergistically with the ester of the unsubstituted or the substituted benzoic acid.

12. A composition according to Claim 11, **characterised** in that the said ester of C_1-C_4 monocarboxylic acid with C_1-C_4 alcohol is the methyl ester, the ethyl ester or the propyl ester of formic acid, acetic acid or propionic acid.

13. A method for preparing the ester composition according to Claim 11 or 12, **characterised** in that the component d) is allowed to be formed in the composition by adding C_1-C_4 alcohol, preferably propanol, to it.

14. A composition according to any of the preceding Claims, **characterised** in that its antimicrobic component contains about 1-30 weight-%, preferably about 5-20 weight-% of water.

15. A composition according to any of the preceding Claims, **characterised** in comprising a fixed carrier in particle form.

16. A composition according to Claim 15, **characterised** in that the weight ratio between the antimicrobic component and the carrier in particle form is in the range of 1:10 - 10:1, preferably in the range of 3:7 - 7:3.

17. A composition according to Claim 15 or 16, **characterised** in that the specific surface of the carrier in particle form is at least about 10, preferably at least 100 m^2/g.

18. A composition according to Claim 15, 16 or 17, **characterised** in that the approximate particle size of the carrier in particle form is 0.01-20, preferably 0.1-2 mm.

19. A composition according to any of Claims 15-18, **characterised** in that the corpuscular substance is selected from the following: inorganic corpuscular substances based on silicium dioxide and/or aluminas, including siliceous earth, moler earth, silicic acid, silica, alumina, bentonite, montmorillonite, perlite, steatite, chlorite, expanded vermiculite, calcium silicate, and zeolites, inorganic salts slightly soluble in water and organic acids, and organic substances such as synthetic polymers, cellulose, cellulose derivatives, lignin, and ligneous derivatives.

20. A composition according to any of Claims 15-19, **characterised** in that the antimicrobic substance is absorbed in the corpuscular substance.

21. A composition according to any of Claims 15-20, **characterised** in that the antimicrobic substance is absorbed in the first part of the corpuscular substance and the substance that generates the hydrolysis of the ester of the unsubstituted or the substituted benzoic acid is absorbed in the second part of the corpuscular substance.

22. A composition according to any of the preceding Claims, **characterised** in comprising:

1) an antimicrobic component containing:

a) about 50-99.8 weight-% of unsubstituted or substituted C_1-C_4 monocarboxylic acid,

b) about 0.2-30 weight-% of unsubstituted or substituted ester of benzoic acid,

c) about 0-20 weight-% of a substance generating the hydrolysis of the ester of the unsubstituted or the substituted benzoic acid,

d) about 0-20 weight-% of the ester of C_1-C_4 monocarboxylic acid with alcohol, affecting synergistically with the ester of the unsubstituted or the substituted benzoic acid,

e) about 0-30 weight-% of water, and

2) a fixed carrier in particle form so that the weight ratio between the antimicrobic component and the solid carrier in particle form substance is in the range of 1:10 - 10:0.

23. The use of the composition according to any of the preceding Claims as a substance that inhibits the growth of hazardous microbes, such as *Salmonella*, in forage materials and preparations, and similar materials.

24. The use according to Claim 23 as a processing matter or an additive of forage material or animal forage.

25. The use according to Claim 23 for preserving green forage or grain, for improving the hygiene of cattle sheds and similar premises, or for disinfecting devices, equipment, and packages.

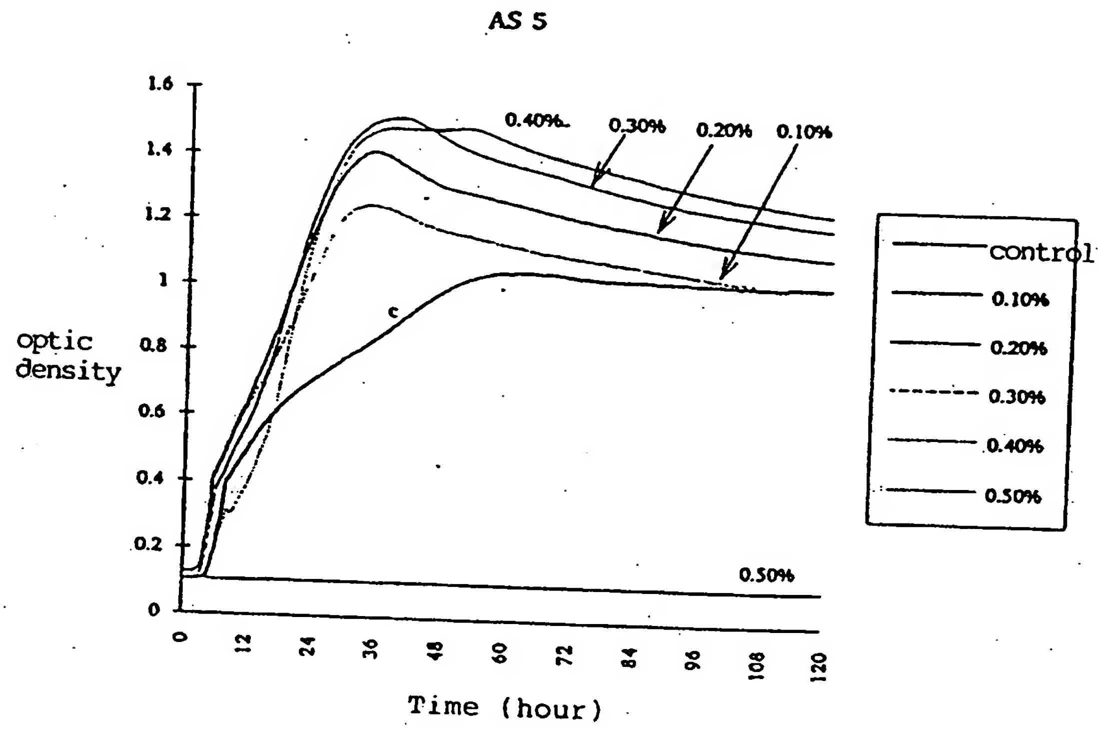

FIG. 1 Acetic acid

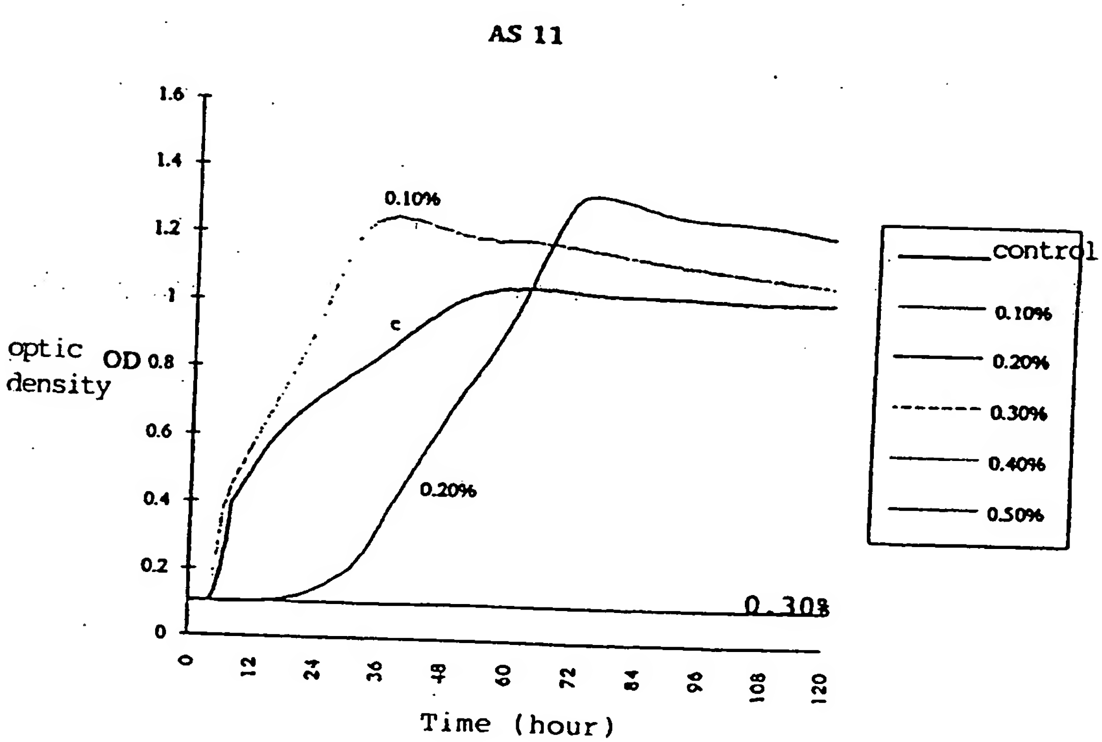

FIG. 2 Acetic acid + 2,5 % EB + 2,5 % PF
(EB = ethyl benzoate, PF = propyl formiate)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 96/00066

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: A01N 37/02, A01N 37/06, A01N 37/10, A23K 3/03, A23L 3/3517
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: A01N, A23K, A23L, A23B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 9221239 A1 (ECOLAB INC.), 10 December 1992 (10.12.92) --	1-25
X	WO 9316603 A1 (KEMIRA OY), 2 Sept 1993 (02.09.93) --	1-25
X	GB 2095534 A (MARTTI EMIL LAMPILA), 6 October 1982 (06.10.82) --	1-25

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 May 1996	07 -05- 1996
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Gerd Strandell Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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